# Study of iron-related complexes in silicon by ESR measurement(Abstracts of Doctoral Dissertations,Annual Report(from April 1999 to March 2000))

# Study of iron-related complexes in silicon by ESR measurement

Toru Takahashi

*Institute for Materials Research*

## 1. INTRODUCTION

Semiconductors are known to be structural-sensitive. It means that their optical and electrical properties strongly depend on impurities and defects contained in them. We studied iron-related complexes in Si. Fe is a main contaminant in Si since it has a high diffusivity even at RT and Fe vapor pressure is usually high due to iron-based apparatus. It degrades electrical properties of Si crystals since it has a deep donor level ($E_V$+0.35 eV, $E_V$: top of the valence band) in band gap.

Fe easily forms complexes with other impurities and defects because of high diffusion rate and multiple charge states (+1, neutral, -1). In this study, we investigated recombination-enhanced reaction of Fe-group III acceptor pairs and geometrical structure of Fe-H complexes based on following background.

Fe-group III acceptor pairs have deep donor levels at about $E_V$+0.1 eV. Such deep states have strong coupling with the lattice, so-called strong electron-phonon coupling, because of small extension of electric wave function. One prominent phenomenon of such system is recombination-enhanced defect reaction (REDR) where atomic movement occurs associated with the recombination of extra electron and holes at defect levels. To understand this phenomenon, we should determine the reduction of migration energy, threshold energy to induce REDR, energy levels relevant to recombination of electrons and holes, and so on. Dissociation of Fe-B and Fe-Al pairs under illumination were investigated. To understand REDR of Fe-acceptor pairs, we performed similar experiment for Fe-Ga and Fe-In pairs in this study.

Many of transition metal (TM) impurities in Si form complexes with H. Energy levels of TM usually change due to complex formation. Sadoh determined the energy level of Fe-H complex from an electrical measurement. Properties of Fe-H complexes such as atomic structure and number of H atoms included in the complexes, however, were not determined. To clarify these properties, we studied Fe-H complexes from the measurement of their ESR (Electron Spin Resonance) spectrum.

## 2. EXPERIMENT

Crystals used in this study were grown by the floating-zone (FZ) grown method. In case of Fe-acceptor pairs, after shaping and chemical polishing of p-type specimens doped with Ga and In with concentrations of $5\times10^{15}$ and $3\times10^{15}$ atoms $cm^{-3}$, respectively, we doped specimens with Fe with the vapor method. The concentrations of Fe were $3\times10^{15}$ and $1.5\times10^{15}cm^{-3}$, for Ga and In doped specimen, respectively. Specimen used in the study of Fe-H complex was n-type Si grown by FZ method doped with phosphorus ($10^{16}cm^{-3}$). After above treatment, Fe and H were doped. H was doped by annealing in hydrogen gas followed by quenching. The concentrations of Fe and H were $10^{14}\sim10^{16}$ atoms $cm^{-3}$. Specimens prepared by the above treatment were measured by ESR method. By this method, .the symmetry of a defect is determined. We needed to know the position of Fe before and after illumination-induced REDR. The site of Fe was determined by considering the symmetry of Fe-acceptor pair. We measured the ESR spectra of Fe-acceptor pairs and Fe-H complex by an X-band spectrometer at 10 K. We illuminated specimens at between 100 and 250 K in the study of REDR of Fe-acceptors.

## 3. RESULTS AND DISCUSSION

### 3.1 REDR of Fe-acceptor pairs in Si.

We observed the Fe atom jump from the first nearest- to the second nearest-neighbor interstitial site of an acceptor atom at low temperature (150 K) under illumination where Fe atom cannot jump without illumination. We determined the activation energy of Fe atom jump from the dependence of ESR intensities of the first and second nearest-neighbor pairs on illuminating temperature (Table 1). The activation energies for Fe atom jump under REDR were much smaller than the activation energy for thermally jump. In addition, we studied the threshold energy of REDR. From the analysis by Lucovsky model, the threshold energy was known to correspond to the electron excitation from the ground state of an isolated acceptor atom to the bottom of conduction band. Hence, we conclude the mechanism of REDR of Fe-acceptor pairs following. An electron is excited from the energy level of an isolated acceptor atom to the bottom of conduction band under illumination. A hole has already been captured by the energy level of Fe-acceptor pair, because the concentration of acceptor atom is higher than the Fe concentration. Then, an electron in the conduction band is captured by acceptor level of Fe-acceptor pair and the electron-hole recombination occurs. The released electronic energy at that time contributes to the Fe atom jump process; the activation energy for the Fe atom jump is reduced.

Finally, we interpreted above results with Sumi's theoretical model on the REDR within complexes. The direction cosine between recombination direction and atomic jump estimated by Sumi's model from the reduction of activation energy agrees well with that determined from the geometrical configuration of Fe acceptor pairs.

Table 1 The activation energy of Fe jump under illumination and dark: (eV)

| | dark | illumination |
|---|---|---|
| Fe-Al | 0.82 | 0.11 |
| Fe-Ga | 0.75 | 0.08 |
| Fe-In | 0.69 | 0.02 |

### 3.2 Fe-H complex in Si.

We doped $^{57}Fe$ (nuclear spin =1/2) for this study. We observed the ESR spectrum of Fe-H complex for the first time. This spectrum is composed of these peaks on the H isotope, the thermal stability and H concentration, we confirmed that these peaks are due to Fe-H complexes. Contrary to our expectation, they have an isotropic g-value which is the same as that of isolated Fe atom. This is a peculiar feature since the symmetry of complexes is usually lower than that of isolated impurities. We interpreted the same symmetry of Fe-H and Fe to be due to fast motion of H atom around Fe.

In addition, we discovered that the interstitial Fe ($Fe_i$) concentration changed by H doping. The $Fe_i$ concentration increases at above 1000 °C and decreases at below 1000 °C by hydrogen doping. We explain this result by considering a substitutional Fe ($Fe_S$) and intrinsic defects induced by the formation of $\alpha$-$FeSi_2$ at above 1000 °C and $\beta$-$FeSi_2$ at below 1000 °C at specimen surface enhanced by annealing in hydrogen gas. Fe in Si is known to occupy at interstitial $T_d$ site. $Fe_S$ was observed only in specimens which were electrons irradiated or ion implanted. H doping effect on the concentration of $Fe_i$ indirectly confirmed the existence of $Fe_S$ in thermal equilibrium. 5d TM, for example Pt or Au, occupies both interstitial and substitutional sites because of the diffusion mechanism (kick- out or dissociative mechanism). Though Fe in Si is known to diffuse with interstitial mechanism, above results suggest a possibility that Fe may also diffuse with other mechanisms the same as those of Pt or Au.

## 4. CONCLUSION

We investigated Fe-acceptor pairs and the Fe-H complex with ESR method. First, we studied REDR of Fe-acceptor pair and confirmed the mechanism of REDR of this system. Second, we investigated the Fe-H complex and determined the atomic configuration. Complexes of H and TM which occupies substitutional sites are intensively investigated by various measurements, but complexes of H and TM which occupies interstitial sites such as Fe-H complex are not so much investigated. Study of complexes of H and 3d TM other than Fe is strongly expected to understand properties of isolated 3d TM themselves.